(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
2 October 2003 (02.10.2003)

PCT

(10) International Publication Number
WO 03/080911 A2

(51) International Patent Classification[7]: D04H

(21) International Application Number: PCT/SG03/00061

(22) International Filing Date: 27 March 2003 (27.03.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/106,033 27 March 2002 (27.03.2002) US

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/080911 A2

(54) Title: ANTIMICROBIAL YARN HAVING NANOSILVER PARTICLES AND METHODS FOR MANUFACTURING THE SAME

(57) Abstract: The present invention provides a method for making the antimicrobial yarn. The present invention also provides a yarn with antimicrobial effects. The antimicrobial antifungal effect of the yarn is derived from nanosilver particles (diameter between 1 and 100 nm) which are adhered to the yarn. The yarn contains fibers which are made of cotton, linen, silk, wool, leather, blending fabric, synthetic fiber, or any combination thereof. The yarn can be used to make cloth to be used particularly for treating patients with burns or wound. The cloth made from the antimicrobial yarn can be further used to make clothes such as underwear, socks, shoe cushions, shoe linings, bed sheets, pillow cases, towels, women hygiene products, laboratory coats, and medical robes.

ANTIMICROBIAL YARN HAVING NANOSILVER PARTICLES AND METHODS FOR MANUFACTURING THE SAME

FIELD OF THE INVENTION

The present invention relates to fabric with a coating of silver particles in the nanometer range. It also relates to a method of making the same.

DESCRIPTION OF THE RELATED ART

Metals including silver, copper, mercury, and zinc are known for anti-bacterial properties. Bacteria treated by these metals do not acquire resistance to the metals. Therefore, the bactericidal metals have advantages over the conventional antibiotics which often cause the selection of antibiotic-resistant microorganism.

Silver is generally a safe and effective antimicrobial metal. Silver ions function in adversely affecting cellular metabolism to inhibit bacterial cell growth. When silver ions are absorbed into bacterial cells, silver ions suppress respiration, basal metabolism of the electron transfer system, and transport of substrate in the microbial cell membrane. Silver has been studied for antibacterial purposes in the form of powder, metal-substituted zeolite, metal-plated non-woven fabric, and crosslinked compound.

Nano technology is the study and treatment of substance and material in a nanometer range. Nanometer equals to 10^{-9} meter. The internationally acclaimed range for research and study for the nano technology is between 0.1 nm and 100 nm. The technology has been applied in the areas of information technology, energy, environment, and biotechnology. Particularly, the technology has been used in medicine including drug carrier, cell dye, cell separation, clinical diagnosis, and disinfection.

In the late eighteenth century, western scientists confirmed that colloidal silver, which had been used in oriental medicine for centuries, was an effective antibacterial

agent. Scientists also knew that the human body fluid is colloidal. Therefore, colloidal silver had been used for antibacterial purposes in the human body. By the early nineteenth century, colloidal silver was considered the best antibacterial agent. However, after the discovery of antibiotics, due to the fact that antibiotics were more potent which could in turn generate more revenue, antibiotics had substituted colloidal silver as the main choice for antibacterial agents.

Thirty years after the discovery of the antibiotics, many bacteria developed resistance to the antibiotics, which became a serious problem. Since 1940s, silver, particularly colloidal silver, has once again been recognized for antibacterial use, particularly due to its ability for not causing drug-resistance.

Antibacterial cloth containing metallic particles (particularly copper, silver, and zinc in the form of zeolite) is known in the field for a long time. Many methods for incorporating the metal ions directly into a cloth or fabric have been proposed. However, in the methods in which the metals are used directly, the incorporation of metals lead to very expensive products, with heavy weights as they are necessarily used in a large amounts.

There are also methods teaching the use of a polymeric substance to hold the metallic ions. For example, the method of binding or adding fine wires or powder of the metals themselves to a polymer and the method of incorporating compounds of the metals into a polymer. However, the products obtained by these methods shows poor durability of antibacterial performance and can be utilized only for restricted purposes because the metal ions are merely contained in or attached to the polymer and, accordingly, they easily fall away from the polymer while being used.

For example, Japanese Patent No. 3-136649 discloses an antibacterial cloth used for washing breasts of milk cow. The Ag^+ ions in $AgNO_3$ are crosslinked with polyacrylonitrile. The antibacterial cloth has demonstrated anti-bacterial activity on six (6) bacterial strains including *Streptococcus* and *Staphylococcus*.

Japanese Patent No. 54-151669 discloses a fiber treated with a solution containing a compound of copper and silver. The solution is evenly distributed on the fiber. The fiber is used as an anti-bacterial lining inside boots, shoes, and pants.

U.S. Patent No. 4,525,410 discloses a mixed fiber assembly composed of low-melting thermoplastic synthetic fibers and ordinary fibers which are packed and retained with specific zeolite particles having a bactericidal metal ion.

U.S. Patent No. 5,180,402 discloses a dyed synthetic fiber containing a silver-substituted zeolite and a substantially water-insoluble copper compound. The dyed synthetic fiber is prepared by incorporating a silver-substituted zeolite in a monomer or a polymerization mixture before the completion of polymerization in the step of preparing a polymer for the fiber.

U.S. Patent Nos. 5,496,860 and 5,561,167 disclose antibacterial fiber including an ion exchange fiber and an antibacterial metal ion entrapped within the ion exchange fiber through an ion exchange reaction. The ion exchange fiber has sulfonic or carboxyl group as the ion exchange group.

U.S. Patent No. 5,897,673 discloses fine metallic particles-containing fibers with various fine metallic particles therein, which have fiber properties to such degree that they can be processed and worked, and which can exhibit various functions of the fine metallic particles, such as antibacterial deodorizing and electroconductive properties as provided.

U.S. Patent No. 5,985,301 discloses a production process of cellulose fiber characterized in that tertiary amine N-oxide is used as a solvent for pulp, and a silver-based antibacterial agent and optionally magnetized mineral ore powder are added, followed by solvent-spinning.

The materials of the prior art involving the use of zeolite do not have sufficiently antibacterial activity due to lack of sufficient surface contact between the bactericidal metal and the bacteria, especially in water. The bactericidal activity of these materials rapidly diminishes as the silver ions become separated from the supports, especially in water. Most importantly, these materials do not show bactericidal activity over a prolonged period of time and the crosslinking may introduce compounds that cause allergy in patients.

There is yet another approach of making antibacterial cloth such as by inserting a layer of metallic yarn between a woven fabric. For example, Japanese laid-open patent publication (unexamined) No. Hei 6-297629 discloses an antibacterial cloth in which an inner layer member containing copper ion in a urethane foam resin is inserted in a cloth-like outer layer member. The outer layer member is composed of a cotton yarn serving as a weft formed by entangling an extra fine metallic yarn of copy or the like and a rayon yarn serving as a warp. A warp is the threads of a woven fabric which are extended longhtwise in the loom. A weft is the threads of a woven fabric that cross from side to side of the web and interlace the warp. This type of antibacterial cloth is heavy and hard. In addition, the extra fine metallic yarn is easy to cut, thus, causing problems to wash the cloth repeatedly. It may also injure a user due to the cut metallic yarn.

Recently, Chinese Patent No. 921092881 discloses a method for making antibacterial fabric with long lasting broad-spectrum antibacterial effect against more than 40 bacteria. The fabric is manufactured by dissolving silver nitrate in water, adding

ammonia water into the solution to form silver-ammonia complex ion, adding glucose to form a treating agent, adding fabric into the treating agent, and ironing the fabric by electric iron or heat-rolling machine. The use of ammonia water in the reaction causes many problems. First, ammonia water has intense, pungent, suffocating odor which irritates skin and mucous membranes of workers. Second, ammonia water causes pollution to the environment.

It is therefore an object of the present invention to provide an improved method for producing antimicrobial fabric that is safe both for the workers and the environment.

SUMMARY OF THE INVENTION

The present invention provides a fibrous material which contains nanosilver particles in the diameter of less than 100nm, e.g. about 1-100 nm. The fibrous material may be cotton yarn, non-woven cotton, cotton wool, gauze, cloth, linen silk, wool, blended fabric, and synthetic fiber. Many of these fabrics contain fibers or yarn and for ease of description, the term "yarn" is used synonymously with the terms "fabric" and "fibrous material". The term "yarn" is therefore used for the ease of description and is not meant to limit the present invention to a long thin fiber.

The present invention provides an antimicrobial yarn having nanosilver particles adhered thereto that is very effective over a broad spectrum of bacteria, fungi, and virus. The antimicrobial fiber of the present invention does not lose the antimicrobial strength over time, and the fiber is especially effective in water. The yarn used in the present invention can contain natural or synthetic fibers; its color can be natural or dyed. The

antimicrobial yarn of the present invention is non-toxic, safe, and thus, suitable for use in healthcare related purposes.

The fibrous material may be completely soaked in the reaction solution and the resulting nanosilver coated material is stable and has good antimicrobial or biocidal activity for at least 6 months, even with at least one hundred washes according to fabric that are normally washable. The total weight of silver in the yarn may be, for example, about 0.2 to 1.5% by weight. The nanosilver particles are adhered to the fibers of the yarn. The resulting nanosilver particles are sized below 100 nm in diameter, e.g. 1-100nm with the diameter staying in the same range for at least 6 months.

In the preferred embodiment, the fibrous material according to the present invention maintains good antimicrobial activity for at least 1 year even with at least one hundred washes according to the method as described in Example 5 below. The nanosilver particles coating the material according to the present invention has particle size below 100 nm with the diameter staying in the same range for at least 1 year.

In the most preferred embodiment, the fibrous material according to the present invention maintains good antimicrobial activity for at least 2 year even with at least one hundred washes according to the method as described in Example 5 below. The nanosilver particles coating the material according to the present invention has particle size below 100 nm, with the diameter staying in the same range for at least 2 year.

In the method according to another aspect of the present invention, the silver of the nanosilver particles is made by reducing silver nitrate with a reducing agent and in the absence of ammonia or ammonia water. The preferred reducing agent is glucose or ascorbic acid (vitamin C).

The yarn has antimicrobial effects against bacteria, fungi, and/or chlamydia, which include, but are not limited to, *Escherichia coli, Methicillin resistant Staphylococcus aureus, Chlamydia trachomatis, Providencia stuartii, Vibrio vulnificus, Pneumobacillus, Nitrate-negative bacillus, Staphylococcus aureus, Candida albicans, Bacillus cloacae, Bacillus allantoides, Morgan's bacillus (Salmonella morgani), Pseudomonas maltophila, Pseudomonas aeruginosa, Neisseria gonorrhoeae, Bacillus subtilis, Bacillus foecalis alkaligenes, Streptococcus hemolyticus B, Citrobacter,* and *Salmonella paratyphi C.*

The antimicrobial yarn can be used to make cloth (such as bandage, gauze, and surgical cloth) with antimicrobial activity, particularly to be used for treating patient with burn and scald-related skin infection, wound-related skin infection, dermal or mucosal bacterial or fungal infection, surgery cut infection, vaginitis, and acne-related infection.

Additionally, the cloth with antimicrobial activity can be used to make antibacterial clothes or clothing such as underwear, socks, shoe cushions, shoe linings, bed sheets, pillow shams, towels, women hygiene products, laboratory coat, and patient clothes.

The present invention also provides a method for manufacturing the antimicrobial yarn. The method includes (1) mixing an aqueous solution of a silver salt such as silver nitrate with a reducing agent to form a silver containing processing solution (which is also referred to as the nanosilver solution) in the absence of ammonia or ammonia water; (2)soaking the yarn in the nanosilver solution to obtain a soaked material; and (3) dehydrating and drying the soaked material to form yarn with antimicrobial activity. Preferably, the yarn is pre-degreased before soaking in the nanosilver solution. Additionally, after dehydrating the soaked material, the yarn can be treated with heat at 120-160°C for about 40-60 minutes. Silver nitrate is the preferred salt because it is has sufficient solubility in an aqueous solution in the absence of ammonia or ammonia water to

allow the above reaction to occur. In another embodiment, silver acetate or silver sulfate may be used.

Also, preferably, the aqueous silver nitrate solution and said aqueous solution of reducing agent are mixed at 0-40°C. The aqueous solution is preferably water solution. For each liter of the nanosilver solution, it is preferred that it contains 2-20 g of silver nitrate, and 1.2-20g of reducing agent, preferably glucose. The silver nitrate and said glucose in the nanosilver solution is preferably at a ratio of about 1 : 0.6 - 1 by weight. The resulting nanosilver particles are sized less than 100nm, e.g. between 1 to 100 nm in diameter. In one of the examples illustrated below demonstrated that the resulting nanosilver particles are sized less than 20nm, e.g. between 1 to 20nm with at least 70% of the nanosilver particles with diameters of less than 10nm, e.g. 1 – 10nm. The antimicrobial yarn contains about 0.2% to 1.5% by weight of silver in a form of attached nanosilver particles.

The method provided herein for making the antimicrobial yarn which is very simple, fast, and easy to carry out. The use of ammonia or ammonia water is completely eliminated in the process of the present invention, thus, the method of the present invention is environmentally safe and non-irritating to workers. The method of the present invention also produces reliable results and can be applied in small and industrial scale production.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a transmission electron micrograph (JEM-100CXII) which shows a yarn evenly attached with nanosilver particles. The diameters of the nanosilver particles were below 20 nm. The total wt% of silver in the yarn was 0.2-1.5%. A: Batch No. 010110; B:

Batch No. 001226; C: Batch No. 001230; D: Batch No. 010322-1; E: Batch No. 011323; F: Batch No. 010322-2.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides an antimicrobial yarn which has a long-lasting effect and a broad-spectrum antimicrobial activity. The antimicrobial yarn contains nanosilver particles having diameters in the range of less than 100 nm, for example, 1-100nm. The nanosilver particles are adhered to the fibers of the yarn and contribute to the antimicrobial effects. The silver content in the antimicrobial fiber is, by way of example, 0.2% to 1.5% by weight of the total weight of the yarn

For ease of description, a range of 1-100nm or 1-10nm etc may also be used to describe the particle size, but it is clear that such a range does not preclude particles that may be formed with diameters of less than 1 nm, as it is generally known that the upper limit of the silver particle size affects the biocidal activity of the material, not the low limit thereof.

The fibers of the yarn are made of cotton, linen, silk, wool, leather, blending fabric, or synthetic fiber or a combination therewith. The yarn can be either in its natural color or dyed with various colors, and the antimicrobial capacity of the yarn (either in natural color or dyed with various colors) is retained.

The antimicrobial yarn of the present invention is non-toxic, safe, and thus, suitable for use in medical or healthcare related purposes. The antimicrobial yarn can be used to make an antimicrobial cloth. The cloth is suitable for use as bandage, gauze, or surgery cloth. It can also be used in making clothes or clothing such as underwear, panty, shoe

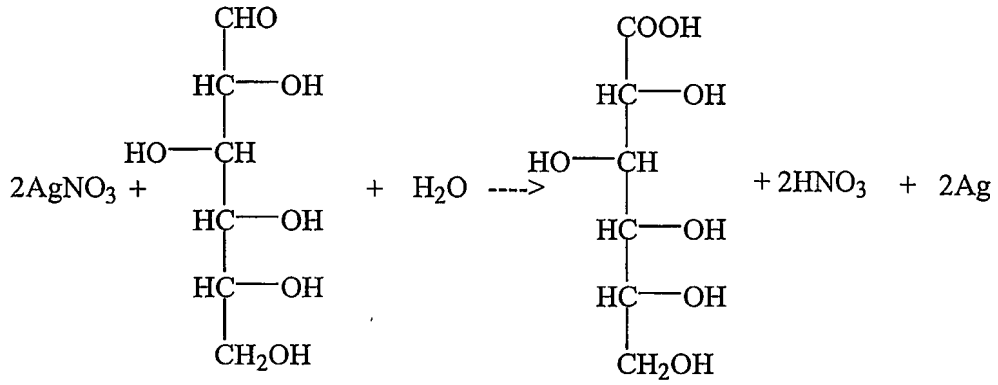
cushions, shoe insole, shoe lining, bedding sheets, pillow sham, towel, feminine hygiene products, medical robes and etc.

The term "antimicrobial" as used in the context of "antimicrobial yarn," "antimicrobial cloth," and/or "antimicrobial clothes or clothing" in the present invention means that the yarn, cloth, or clothes (or clothing) has demonstrated antibacterial, antifungal, and anti-chlamydia effects by killing and/or suppressing growth of a broad spectrum of fungi, bacteria, and chlamydia, such as *Escherichia coli, Methicillin resistant Staphylococcus aureus, Chlamydia trachomatis, Providencia stuartii, Vibrio vulnificus, Pneumobacillus, Nitrate-negative bacillus, Staphylococcus aureus, Candida albicans, Bacillus cloacae, Bacillus allantoides, Morgan's bacillus (Salmonella morgani), Pseudomonas maltophila, Pseudomonas aeruginosa, Neisseria gonorrhoeae, Bacillus subtilis, Bacillus foecalis alkaligenes, Streptococcus hemolyticus B, Citrobacter,* and *Salmonella paratyphi C.*

The antimicrobial effect of the present invention is derived from silver ions which have advantage over the conventional antibiotics, as it does not induce resistance in the microorganisms. The antimicrobial yarn of the present invention does not lose the antimicrobial strength over time, and the antimicrobial effects are especially stronger in water.

Specially, the antimicrobial yarn of the present invention is suitable for use as cloth or clothes in disinfecting and treating patient with burn and scald-related skin infection, wound-related skin infection, skin or mucosa bacterial or fungal infection, surgery cut infection, vaginitis, and acne-related infection.

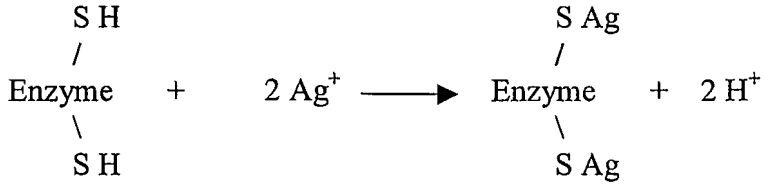
The antimicrobial activity of the nanosilver particle can be explained by the following scheme using silver nitrate as the substrate and glucose as a reducing agent:



Glucose Gluconic Acid

As shown above, the silver nitrate is reduced to metallic silver by interacting with glucose (where the glucose itself is oxidized to gluconic acid). It is important to note that the present invention does not use ammonia or ammonia water.

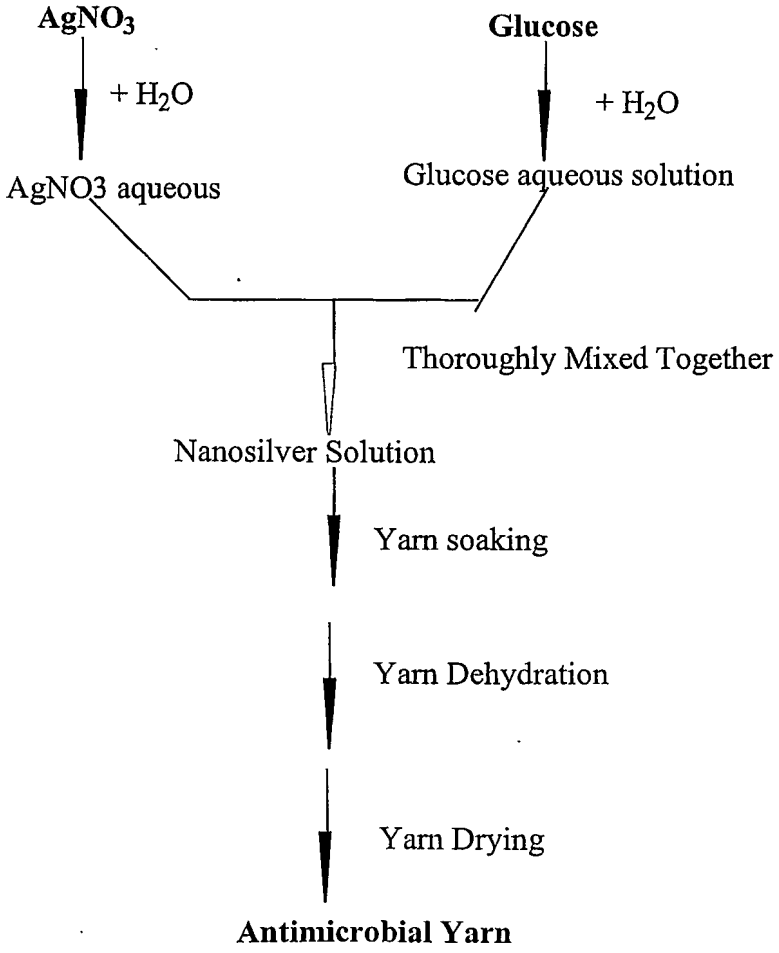
The antimicrobial activity of the silver can further be explained by the following reaction:



Silver nitrate is one of the most powerful chemical germicides and is widely used as a local astringent and germicide. However, the nitrates irritate the skin. Thus, it is preferable to reduce the silver nitrate to metallic silver. When the metallic silver is in contact with an oxygen metabolic enzyme of a microorganism, it becomes ionized. And,

as shown in the above reaction, the silver ion interacts with the sulfhydryl group (-SH) of the enzyme in the microorganism and forms an -SAg linkage with the enzyme, which effectively blocks the enzyme activity.

The antimicrobial yarn of the present invention is prepared according to the following flow chart:



First, dissolving silver nitrate and a reducing agent respectively in water to form an aqueous solution of silver nitrate and an aqueous solution of the reducing agent. It is noted that a direct mixing of the solid forms of silver nitrate and reducing agent in an aqueous solution is not encouraged because it may result in an uncontrollable reaction. The aqueous solution of silver nitrate is then mixed and stirred with the aqueous solution of the reducing agent at 0-40°C, preferably below 25°C. The nanosilver solution is used as the

soaking solution for the yarn. The reducing agent can be glucose or ascorbic acid (vitamin C) preferably, glucose. For 200 kg of yarn, about 1- 4 kg of silver nitrate, about 0.6-3 kg of glucose, and about 500 L (litres) of water are required.

The yarn is preferred to be de-greased prior to the soaking. The degreased process for the yarn is commonly known in the art. After soaking in the nanosilver containing solution for an appropriate period of time, the soaked yarn is dehydrated followed by drying under heat. In this way, every surface of the yarn or fiber has a chance to contact the nanosilver solution, and the resulting nanosilver particles coated thereon are evenly distributed onto all the surfaces of the fibrous material, and not on only one side.

The resulting antimicrobial yarn has advantages of long-lasting effect, broad spectrum antimicrobial activity, non-toxic, non-stimulating, natural, and suitable for medicinal uses. The antimicrobial activity of the yarn is stronger when in water. Because ammonia or ammonia water is not used in the process for making the antimicrobial fiber, the process is more environmentally friendly and safer for workers. The process of the present invention is suitable for both small scale and industrial scale production. It is clear from the above non-limiting examples that numerous embodiments and variations may be produced and used according to the teaching provided herein, for example, the step of soaking the yarn in the nanosilver solution can be replaced with a step of spraying the nanosilver solution to the yarn by a jet sprayer in the preparation of the antimicrobial fabric. The antimicrobial fabric or yarn itself may be used for the medical industry or any other industry that benefits from yarn with antimicrobial activiy for medical purposes or other uses not described here. It is intended that the scope of the invention be defined by the claims appended hereto and their equivalents. The following examples are illustrative, and should not be viewed as limiting the scope of the present invention. Reasonable

variations, such as those occur to reasonable artisan, can be made herein without departing from the scope of the present invention.

EXAMPLE 1

Preparation of the Small Scale of Antimicrobial Yarn

(1) Preparation of Nanosilver Solution:

(a) *Silver nitrate solution*:

$AgNO_3$ 3.9 g

Dissolved in 150 ml of Water

(b) Reducing solution:

Glucose 2.4 g

Dissolved in 100 L of Water

The nanosilver solution was prepared by mixing the silver nitrate solution with the reducing agent solution thoroughly at room temperature (25°C).

(2) Preparation of antimicrobial yarn:

The antimicrobial yarn was prepared as follows:

(i) Naturally white, degreased yarns (50 g) were immersed in the nanosilver solution of (1). The yarns were squeezed and rolled in the solution so that the yarns were fully absorbed with the nanosilver solution.

(ii). The nanosilver solution was partly removed from the yarns by centrifugation (such as in a washing machine) and dried in an oven at 120 -160°C.

(iii). The dried yarns were washed by water, dehydrated, and dried again in the oven to obtain the antimicrobial yarn of the present invention which showed an orange color.

EXAMPLE 2

Preparation of Industrial Scale of Antimicrobial Yarn l

(1) Preparation of Nanosilver Solution

(a) *Silver nitrate solution*:

$AgNO_3$ 5.5 kg

Dissolved in 250 L of Water

The silver nitrate aqueous solution was prepared by dissolving 5.5 kg of silver nitrate in 250 L of water at room temperature in a 500-litre container.

(b) *Reducing solution*:

Glucose 5.7 kg

Dissolved in 150 L of Water

The aqueous solution of Glucose was prepared by dissolving 5.7 kg of glucose at room temperature in 150 L water in a 200-litre container to form an aqueous solution of glucose.

(c) *Nanosilver solution*:

The nanosilver solution was prepared by mixing the silver nitrate solution with the reducing agent solution. Additional water, with stirring, was added to the mixture at room temperature to make the volume up to 500 L.

(2) Preparation of antimicrobial yarn:

The antimicrobial yarn prepared as follows:

(i). Naturally white, degreased yarns (200 kg) were immersed in the nanosilver solution of (1). The yarns were squeezed and rolled in the solution so that the yarns were fully absorbed with the nanosilver solution.

(ii). The nanosilver solution was partly removed from the yarns by dehydration such as using centrifugation. The yarn was further dried in an oven at 120 -160°C for about 40-60 minutes.

(iii). The dried yarns were washed by water, dehydated and dried again in the oven to obtain the antimicrobial yarn of the present invention which showed a yellow-orange color.

The advantage of the above two embodiments (Example 1 and Example 2) is that the use of ammonia or ammonia water is completely eliminated in the process, thus, these embodiments are environmentally safe and non-irritating to workers.

EXAMPLE 3

Electron Microscopic Studies of the Antimicobial Yarn

(1) Purpose:

The yarn produced by the method described in Example 1 was analyzed for the dimension and distribution of nanosilver particles attached.

(2) Method:

Five samples of the antimicrobial yarn prepared in Example 1 (supra) was examined according to the procedure described in the JY/T011-1996 transmission electron microscope manual. JEM-100CXII transmission electron microscope was used with accelerating voltage at 80 KV and resolution at 0.34 nm.

(3) Results:

As shown in Figure 1, all six batches of the antimicrobial yarn samples contained nanosilver particles which were evenly distributed to the yarn. Batch No. 010110 (Fig.

1A) contained about 62% of nanosilver particles that were under 10 nm in size, about 36% that were about 10 nm in size, and about 2% that were 15 nm in size. Batch No. 001226 (Fig. 1B) contained about 46% of nanosilver particles that were under 10 nm in size, about 47% that were about 10 nm in size, and about 7% that were about 15 nm in size. Batch number 001230 (Fig. 1C) contained about 65% of nanosilver particles that were under 10 nm in size, about 24% that were about 10 nm in size, and about 11% that were about 15 nm in size. Batch No. 010322-1 (Fig. 1D) contained about 89% of nanosilver particles that were under 10 nm in size, about 8% that were about 10 nm in size, and about 3% that were about 15 nm in size. Batch No. 011323 (Fig. 1E) contained about 90% of nanosilver particles that were under 10 nm in size, about 7% that were about 10 nm in size, and about 3% that were about 15 nm in size. Batch No. 010322-2 (Fig. 1F) contained 70% of nanosilver particles that were under 10 nm in size, about 12% that were about 10 nm in size, and about 13% that were about 15 nm in size. Chemical testing indicated that the silver content in the yarn was about 0.4-0.9% by weight.

(4) Conclusion:

The results as shown in Figure 1 demonstrated that the antimicrobial yarn contained nanosilver particles with diameters below 20 nm. These nanosilver particles were evenly distributed to the yarn.

EXAMPLE 4

Broad Spectrum of Antimicrobial Activity of the Antimicrobial Yarn

(1) Purpose:

The antimicrobial yarn prepared in Example 1 was examined to determine the antimicrobial activity of the yarn.

(2) Method:

Both the antimicrobial yarn of the present invention (the experimental group) and the yarn without the attachment of nanosilver particles (the control group) were tested in the test tubes. Microbial strains tested were *Escherichia coli, Methicillin resistant Staphylococcus aureus, Chlamydia trachomatis, Providencia stuartii, Vibrio vulnificus, Pneumobacillus, Nitrate-negative bacillus, Staphylococcus aureus, Candida albicans, Bacillus cloacae, Bacillus allantoides, Morgan's bacillus (Salmonella morgani), Pseudomonas maltophila, Pseudomonas aeruginosa, Neisseria gonorrhoeae, Bacillus subtilis, Bacillus foecalis alkaligenes, Streptococcus hemolyticus B, Citrobacter,* and *Salmonella paratyphi C.* These strains were either isolated from clinical cases or purchased as standard strains from Chinese Biological Products Testing and Standardizing Institute.

Two sets of test tubes, each containing a triplicate of various microbial strains were prepared by inoculating the microbial strains into the test tubes containing a meat broth. Then, equal weights of the yarns from the present invention and from the control were inserted into the test tubes. The test tubes were then cultured at 37°C for 18-24 hours. At the end of the incubation, an aliquot of the broth from each of the test tube was taken out and spread onto a Trypticase soy blood agar plate. The blood agar plate was incubated at 37°C for 18-24 hours.

(3) Results:

No colony or sign of any microbial growth was observed on the blood agar plate of the experimental group, as opposed to those of the control group where signs of microbial growth were seen.

(4) Conclusion:

The antimicrobial yarn of the present invention demonstrated effective antimicrobial activity against various bacteria, fungi, and chlamydia.

EXAMPLE 5

Long Lasting Effect of Antimicrobial Activity of the Antimicrobial Yarnl

(1) Purpose:

The antimicrobial yarn of Example 1 of the present invention was examined for the antimicrobial activity over a prolonged period of time. The antimicrobial activity of the yarn after repeated washes was also conducted.

(2) Method:

The antimicrobial yarn of the present invention was washed according to the washing Procedure as provided in the Functional Treatment of the Fabric, Chinese Textile Publishing House (January 2001) as follows:

(i) 2 g of neutral soap solution (1:30) was dissolved in one litre of water to obtain a wash fluid;

(ii) A yarn from the experimental group or the control group as described in Example 4 was washed using the wash fluid of (i) at room temperature for 2 minutes;

(iii) The yarn was rinsed in water;

(iv) After every five washes in the wash fluid, the yarn was dried at 60°C.

(v) After 100 times of washing procedure according to (i) to (iv), nine batches of antimicrobial yarn were tested for antimicrobial activity on *Staphylococcus aureus*, *Escherichia coli*, *Candida albicans*, and *Pseudomonas aeruginosa* according to the method provided in Example 4.

(3) Results:

No colony or any signs of microbial growth were observed in the yarn of the experimental group, as opposed to those in the control group where signs of microbial growth were observed.

(4) Conclusion:

The above results indicate that the yarn of the present invention was very effective and long lasting as antimicrobial agent even after repeated washes.

EXAMPLE 6

Antimicrobial Activity of the Antimicrobial Yarn Made with Different Materials or Dyed with Different Colors

(1) Purpose:

The antimicrobial activity of the antimicrobial yarn of the present invention prepared from different materials or dyed with various colors was examined.

(2) Method:

(i) The yarn (from the experimental group or the control group) which was made from cotton, linen, silk, wool, leather, blending fabric, or synthetic fiber, or which was dyed in black, blue, red, orange, and yellow was prepared.

(ii) The yarns of (i) were tested for antimicrobial activity on *Staphylococcus aureus*, *Escherichia coli*, *Candida albicans*, and *Pseudomonas aeruginosa*, according to the method provided in Example 4.

(3) Results:

No colony or any signs of microbial growth were observed in the yarn of the experimental group, as opposed to those in the control group where signs of microbial growth were observed.

(4) Conclusion:

The antimicrobial yarn of the present invention made from different materials, which included cotton, linen, silk, wool, leather, blending fabric, or synthetic fiber, or dyed with different colors, was very effective as antimicrobial agent, suggesting the materials or dying methods would not and did not hinder the antimicrobial activity of the nanosilver particles-containing yarn.

Although the instant invention has been described using the above-mentioned examples, these examples are meant for illustration only and are not intended to limit the scope of the invention. Specifically, the fibrous material according to the present invention may be fibers or yarns that may be woven into various materials and may be used for lining in gloves and surgical masks. The surgical masks may be single plied or multi-plied and the nanosilver fabric may be in all plies or only one of the plies in the mask. The method may also be applied to one or both sides of a leather material, for example for antimicrobial shoes with an inner lining of nanosilver coating. In the absence of ammonia, the workers will be protected from the toxic fume and the leather material will also be protected from the ammonia effect.

We claim:

1 A fibrous material comprising nanosilver coating comprising nanosilver particles having diameters below 100nm in diameter; wherein said nanosilver particles are coated onto all surfaces of said fibrous material and said nanosilver particles remain in said diameter range for at least 6 months.

2 A fibrous material according to claim 1 wherein said material further contains antimicrobial activity and maintain their antimicrobial activity after at least 100 washes according to the method described in Example 5.

3 A fibrous material according to claim 2 wherein said material further contains antimicrobial activity and maintain their antimircobial or biocidal activity for at least 2 years after at least 100 washes.

4 A fibrous material according to claim 1 wherein the silver content of said material is about 0.2 to 1.5% by weight of silver based on the total weight of said material.

5 A fibrous material according to claim 1 wherein the nanosilver particles of said material have diameters below 20nm.

6 A fibrous material according to claim 1 wherein at least 70% of the nanosilver particles of said material have diameters below 10nm.

7 A fibrous material according to claim 2 wherein said material is made of at least one selected from the group consisting of cotton yarn, non-woven cotton, cotton wool, gauze, cloth, linen, silk, wool, leather, blended fabric, and synthetic fiber.

8 A fibrous material according to claim 7 wherein said non-woven cotton is further pressed to form a cloth material.

9 A fibrous material according to claim 1 wherein said material is in natural color or dyed with different color.

10 A fibrous material according to claim 1 wherein said material inhibits growth of bacteria, fungi, or chlamydia.

11 A fibrous material according to claim 7 wherein said material is used to fabricate, apparel, face mask or a portion thereof, underwears, socks, shoe cushions, shoe linings, bed sheets, pillow shams, towels, women hygiene products, laboratory coat, medical robes and the inner lining of gloves.

12 A method of producing a nanosilver material comprising :

a) mixing an aqueous solution of silver nitrate with a reducing agent to form a nanosilver solution in the absence of ammonia or ammonia water;

b) soaking said material in said nanosilver solution to obtain a soaked material; and

c) dehydrating and drying said soaked material to form said nanosilver material having a coating of silver particles thereon.

13 The method according to claim 11, wherein said silver salt is silver nitrate.

14 The method according to claim 12 wherein said material is pre-degreased before soaking in said nanosilver solution.

15 The method according to claim 12 wherein said soaking step (b) is replaced with spraying said nanosilver solution onto said material.

16 The method according to claim 12, further comprising a step of treating said nanosilver material with heat at 120-160°C for about 40-60 minutes.

17 The method according to claim 15, wherein said reducing agents is glucose or ascorbic acid (vitamin C).

18 The method according to claim 12, wherein each liter of said nanosilver solution comprises 2-20 g of silver nitrate and 1.2-20 g of reducing agent.

19 The method according to claim 17, wherein said silver nitrate and said glucose is at a ratio of about 1 : 0.6 - 1 by weight.

20 A face mask comprising a cover portion and an attachment portion for attaching said cover portion onto the face of a user, said cover portion having at least one ply of fabric material with a nanosilver coating comprising nanosilver particles of less than 100nm diameter.

21 A face mask according to claim 19 wherein said cover portion comprises at least two plies, with at least one of the ply having said nanosilver coating.

22 A face mask according to claim 19 wherein said cover portion comprises three plies stacked theretogether with the middle ply having said nanosilver coating.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
2 October 2003 (02.10.2003)

PCT

(10) International Publication Number
WO 2003/080911 A3

(51) International Patent Classification[7]: D06M 11/83

(21) International Application Number:
PCT/SG2003/000061

(22) International Filing Date: 27 March 2003 (27.03.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/106,033 27 March 2002 (27.03.2002) US

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

(88) Date of publication of the international search report:
18 March 2004

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ANTIMICROBIAL YARN HAVING NANOSILVER PARTICLES AND METHODS FOR MANUFACTURING THE SAME

(57) Abstract: The present invention provides a method for making the antimicrobial yarn. The present invention also provides a yarn with antimicrobial effects. The antimicrobial antifungal effect of the yarn is derived from nanosilver particles (diameter between 1 and 100 nm) which are adhered to the yarn. The yarn contains fibers which are made of cotton, linen, silk, wool, leather, blending fabric, synthetic fiber, or any combination thereof. The yarn can be used to make cloth to be used particularly for treating patients with burns or wound. The cloth made from the antimicrobial yarn can be further used to make clothes such as underwear, socks,

WO 2003/080911 A3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG 03/00061-0

CLASSIFICATION OF SUBJECT MATTER

IPC[7]: D06M 11/83

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC[7]: D06M; D06Q

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI; EPODOC; PAJ

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Date of the actual completion of the international search	Date of mailing of the international search report
30 July 2003 (30.07.2003)	11 September 2003 (11.09.2003)
Name and mailing adress of the ISA/AT Austrian Patent Office Dresdner Straße 87, A-1200 Vienna	Authorized officer HAUSWIRTH F.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG 03/00061-0

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